

DATE: February 22, 2006

FILE REF:

TO: Ed Miller – SER
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FROM: Mark K. Allen – AM/7

SUBJECT: 2006 Enhanced Ozone Monitoring Plan (Ground Level Monitoring)

The 2006 monitoring program will be the thirteenth official year of Enhanced Ozone Monitoring (EOM) as required by the 1990 Clean Air Act Amendments and the revised 40 CFR Part 58. For Wisconsin, the 2006 program will also be continuation of ozone precursor monitoring conducted since 1992. The 2006 program uses both established and proven monitoring methods. The 2006 program will continue to improve the operation of the newest analytical systems. These new analytical systems have provided better information on VOCs and oxides of nitrogen. PAMS monitoring is now focused at the DNR's Headquarters supersite. The reduction in monitoring and consolidation of older PAMS sites allows Wisconsin to focus on newer monitoring technologies while still maintaining the collection of critical PAMS data.

The Wisconsin EOM program is part of a Lake Michigan Regional EOM program conducted by the states of Illinois, Indiana, Michigan, and Wisconsin. The Lake Michigan Photochemical Assessment Monitoring Station (PAMS) network has consisted of two components. The first fulfills the requirements of the Lake Michigan Alternative PAMS Plan as approved by USEPA in 1993, and the second includes supplemental measurements and activities developed and implemented by the four states to support the Lake Michigan Data Analysis Plan, photochemical modeling and air quality analysis efforts.

The Wisconsin PAMS Network includes three monitoring sites. One urban source region site located in Milwaukee and two rural downwind sites located at Harrington Beach State Park and in the Woodland Dunes Conservancy near Manitowoc. These three sites are a subset of 33 fixed ozone sites located throughout Wisconsin. The operation of the ozone-monitoring network is carried out as part of the routine monitoring work of the Department Air Monitoring Program and will not be addressed in this plan.

1. Monitoring Objectives

Enhanced Ozone Monitoring will be conducted to obtain information on ambient concentrations of photochemically active VOCs, carbonyl species, and oxides of nitrogen that act as precursors to the formation of ozone. The VOCs, carbonyl species, and the oxides of nitrogen species to be collected and monitored are listed in Table 1(a, b, & c). The monitoring objectives for the Wisconsin PAMS network are put forward in Lake Michigan Data Analysis Plan, Version 1.3. These objectives are summarized below.

- Policy Objectives are to provide information:
 - on current ozone attainment status;
 - trends in ozone concentrations; and
 - effectiveness of ozone control programs.

- Technical Objectives are to:
 - assess the reasonableness of ozone precursor emissions inventories; and
 - provide an improved understanding of ozone formation and transport.

2. General Considerations

a. Siting

Monitoring and Sample collection will be conducted at the three PAMS sites listed below. Parameters measured at the site are listed in Table 2.

Milwaukee – SER Headquarters (AIRS#55-079-026) Beginning in 2001 the SER Headquarters site became the primary PAMS Type 2 site. The station is a monitoring supersite with parameters including VOC species, carbonyl species, ozone, oxides of nitrogen, carbon monoxide, and particulate matter.

Harrington Beach site (AIRS#55-089-0009) The Harrington Beach Station is the designated intermediate site (Type 3; located between the maximum precursor emissions and the maximum ozone). Measurement of oxides of nitrogen will be discontinued at this site in 2006. The site will remain as an important ozone monitoring site.

Manitowoc - Woodland Dunes site (AIRS#55-071-0007) The Manitowoc Station is designated a maximum ozone site (Type 4). This monitoring site focuses on the enhanced monitoring of the oxides of nitrogen.

b. Analyzer Operations

- i. Ozone analyzers will operate at all sites at least for the period from April 15, 2006, until October 15, 2006.
- ii. Oxides of nitrogen analyzers will operate for at least the months of June, July, and August 2006.
- iii. The AutoGC system will operate for at least the months of June, July, and August 2006.

c. Routine Sampling Schedule (See Table 3(a) - 24 Hour Samples)

i. Milwaukee – SER Headquarters

Samples will be collected on an every sixth day schedule beginning on January 5, 2006 and continuing until December 31, 2006. All samples will be collected from 0000 to 2400 Central Standard Time (CST). Each daily sample will consist of both a canister sample for VOCs and a cartridge sample for carbonyl species.

d. Intensive Sampling Schedule (See Table 3(b) - 3 Hour Samples)

i. Milwaukee SER Headquarters

Hydrocarbons will be measured using the AutoGC system. Carbonyl samples will be collected on an every third day schedule beginning on May 29, 2006 and continuing until August 30, 2006. On each sampling day 4-three hour samples will be collected at the site. Sampling times will be 2300 to 0200, 0500 to 0800, 1100 to 1400 and 1400 to 1700 CST. Collection of the overnight sample begins at 2300 CST on the day previous to the sampling day (or midnight of the sampling day CDT).

ii. Forecasted Sampling days

No forecasted sampling is planned for 2006.

iii. Canister Back-up Sampling

While the AutoGC system is the primary monitor for VOCs. In the event that the AutoGC system fails, canister samples will be used to provide a minimum amount of VOC data. Canister samples will be collected on the hours and days listed in the Table 3(b) if the AutoGC system is inoperative for a period of more than 12 hours.

e. Special Study

No special studies related to the PAMS network are planned for 2006.

f. Operations

I will serve as the overall Project Manager for VOC/carbonyl monitoring and will provide general assistance in all areas of the monitoring project; David Grande will assist me in this effort. Specific task responsibilities follow:

Task #1 - Samples Collection

The Southeast District Field Staff will be responsible for the collection of samples and general site operations. This will include the collection of quality control samples (blanks, duplicates, collocates, and spikes). The project manager will take the lead in seeing that this task is accomplished.

David Estano (LMD) will be responsible for the general site operations at the Manitowoc site. This will include the operations of the site ozone analyzer, oxides of nitrogen analyzers (NO_x and NO_y), and meteorological monitoring equipment.

Mary Mertes (LMD) will be responsible for the general site operations at the Milwaukee Headquarters site. This will include the operations of the site ozone analyzer and oxides of nitrogen analyzers (NO_x and NO_y).

Task #2 - Auto GC Operation

Mark Allen and David Grande will take the lead in the daily operating of the Auto GC system. This will include developing a list of all necessary routine checks on the instrument, maintenance schedules and supporting system (gases, et.). The Southeast District Field Staff will assist in collecting operational data on the GC system. David Grande will conduct the primary review of all chromatograms.

Mark Allen will act as the technical lead for the operation of the AutoGC system. This will include resolving technical questions and issues involving sampling and analysis by the AutoGC. This also includes insuring data comparability with: (1) the canister data from analysis at the State Laboratory of Hygiene; (2) AutoGC data from the states of Illinois, Michigan, and Indiana.

Task #3 - WDNR/Wisconsin State Laboratory of Hygiene Coordination

Mark Allen will be responsible for the coordination of samples between the laboratory and the field.

Mark Allen and David Grande will be responsible for resolving technical questions on sampling and analysis.

Task #4 - Canister analysis

The SLOH-Environmental Sciences Section will analyze whole air samples, collected in canisters, for hydrocarbons by gas chromatography with flame ionization detection (GC/FID).

Task #5 - Cartridge analysis

The SLOH - Occupational Health Laboratory will analyze exposed DNPH coated cartridges for carbonyl species using high performance liquid chromatography (HPLC).

Task #6 - Quality Assurance

Steve Schuenemann and Mark Allen will be responsible for QA activities on the monitoring project. These activities will include; Sampling and analysis QC objectives as outlined in Quality Assurance Project Plan; and QA activities developed to support the regional efforts.

David Grande will be responsible for conducting and reporting on internal performance audits (zero audits). This will include checks of air sampling rates.

The PAMS network handbook is available for use by monitoring personnel. Additional copies of the handbook are placed at each PAMS site. Steve Schuenemann will be responsible for approving and disseminating updates to that handbook (similar to the general Air Monitoring Handbook).

Task #7 - Data Management

Jim Hughes will provide overall responsibility for the management of data collected on the PAMS network. Anthony Bowers will be responsible for overseeing the collection of the field data in the Southeast district.

Donalea Dinsmore will be responsible for managing the PAMS databases, final review and correctness of the data, and coordinating the transmission of the data to the U.S. Environmental Protection Agency AIRS database.

Task #8 - Data Analysis and Reporting

Data analysis will be coordinated with LADCO and the state of Illinois, Indiana, Michigan, and Wisconsin. Mark Allen will coordinate this data reporting. David Grande, the central office data subunit and the Southeast Regional Data staff will assist.

Task #9 - Training

David Grande will coordinate training of the site operators for the program.

3. *Monitoring Plan Specifics*

a. Quality Assurance

Quality assurance objectives, activities and goals for 2002 VOC monitoring program will be conducted according to *QA 12.0 Milwaukee Ozone Precursor Monitoring*. This is a draft Quality Assurance Project Plan with approval from the Monitoring QA Coordinator and the Monitoring Section Chief. A copy of the plan is included in the PAMS handbook.

The Lake Michigan States together USEPA Region 5 and LADCO have developed a Quality Assurance Plan for the Regional PAMS Network including quality control activities for AutoGCs. Wisconsin will use the quality assurance objectives, activities and goals developed for the Regional Network.

b. Sample Collection Operating Procedures

Twenty-four hour canister and cartridge samples will be collected following the procedures in OP.11.0 of the Wisconsin Air Monitoring Handbook, *Operation of the Automated Combination Canister and Cartridge Sampler*. Three hour canister and cartridge samples will be collected following the procedures in OP.11.1 of the Wisconsin Air Monitoring Handbook, *Operation of the Automated Multi-Port Canister and Cartridge Sampler*. Copies of both operating procedures are included in the PAMS handbook.

c. Sample Analysis

Analysis of all canister samples will follow the protocol set forth in the laboratory's manual *Organic Chemistry -- Air Analysis Section -- 1910 C₂ - C₁₂ Hydrocarbons in Ambient Air*. Carbonyl analysis will follow the WOHL's protocols.

d. Sampling Schedule

The sampling schedule for the project is given in Tables 3(a) & 3(b).

e. Data Management

All continuous monitoring data will be collected and managed by the Central Office Data subunit and the Southeast Regional Data staff using WISARDS.

The samplers used at the PAMS sites automatically collect the sampling data. This sampling data will be routinely downloaded over phone lines to the AMPAMS fileservice on the CENTRAL. After editing sampling field data will then in-turn be downloaded to the WISARDS data system. Laboratory data will be electronically transferred through the DNR's laboratory portal to the WISARDS data system. An adjunct repository of all laboratory and field data will be an ACCESS file on AMPAMS file service of CENTRAL.

Reviewed data will be processed by WISARDS for submission to the EPA's AQS database.

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Air Monitoring Section Staff

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Attachments

| TABLE 1: 2006 PAMS Target Compounds | | | |
|--|------|-----------------------------------|------|
| (a.) Volatile Organic Compounds | | | |
| 1,2,3-trimethylbenzene | c,gc | Cyclopentene | c |
| 1,2,4-trimethylbenzene | c,gc | Ethane | c,gc |
| 1,3,5-trimethylbenzene | c,gc | Ethylbenzene | c,gc |
| 1,3-butadiene | C | Ethylene | c,gc |
| 1-hexene | c,gc | Isobutane | c,gc |
| 1-pentene | c,gc | Isobutene/1-butene | c,gc |
| 2,2,4-trimethylpentane | c,gc | Isopentane | c,gc |
| 2,2-dimethylbutane | c,gc | Isoprene | c,gc |
| 2,3,4-trimethylpentane | c,gc | Isopropylbenzene | c,gc |
| 2,3-dimethylbutane | c,gc | m-diethylbenzene | c,gc |
| 2,3-dimethylpentane | c,gc | m-ethyltoluene | c,gc |
| 2,4,4-trimethyl-1-pentene | | m-xylene & p-xylene | c,gc |
| 2,4-dimethylpentane | c,gc | Methylcyclohexane | c,gc |
| 2,5-dimethylhexane | C | Methylcyclopentane | c,gc |
| 2-methyl-1-butene | C | n-butane | c,gc |
| 2-methyl-1-pentene | C | n-decane | c,gc |
| 2-methyl-2-butene | C | n-heptane | c,gc |
| 2-methylheptane | c,gc | n-hexane | c,gc |
| 2-methylhexane | c,gc | n-nonane | c,gc |
| 2-methylpentane | c,gc | n-octane | c,gc |
| 3-methyl-1-butene | C | n-pentane | c,gc |
| 3-methylheptane | c,gc | n-propylbenzene | c,gc |
| 3-methylhexane | c,gc | n-undecane | c,gc |
| 3-methylpentane | c,gc | o-ethyltoluene | c,gc |
| 4-methyl-1-pentene | C | o-xylene | c,gc |
| Acetylene | c,gc | p-diethylbenzene | c,gc |
| Benzene | c,gc | p-ethyltoluene | c,gc |
| Cis/trans-2-butene | c,gc | Propane | c,gc |
| Cis/trans-2-hexene | C | Propylene | c,gc |
| Cis/trans-2-pentene | c,gc | Styrene | c,gc |
| Cyclohexane | c,gc | Toluene | c,gc |
| Cyclopentane | c,gc | | |
| PAMHC | | | gc |
| Total nonmethane hydrocarbons | | | c,gc |
| Total unidentified hydrocarbons | | | c |
| Total unidentified hydrocarbons eluting after toluene | | | c |
| Total unidentified hydrocarbons eluting before toluene | | | c |
| Key: | | | |
| c –canister sample species, gc - AutoGC species | | | |
| (b.) Carbonyls | | | |
| Acetaldehyde | | | |
| Acetone | | | |
| Formaldehyde | | | |
| (c.) Oxides of Nitrogen | | | |
| Nitric oxide (NO) | | NOy (total oxides of nitorgen) | |
| Nitrogen dioxide (NO ₂) | | NOz (reactive oxides of nitrogen) | |
| Total Nitric oxide/Nitrogen dioxide (NOx) | | | |

Table 2: PAMS Monitoring Sites

| | Ozone | NOx | NOy | VOC | Carbonyls | Met. |
|------------------------|-------|------------------|-----|--------|-----------|------|
| Milw. DNR Headquarters | X | High sensitivity | X | AutoGC | X | X |
| Harrington Beach | X | | | | | X |
| Manitowoc | X | High sensitivity | X | | | X |

Table 3(a): PAMS Baseline (24-hour) Sampling Schedule

[illegible]

| Sampling Schedule Code Key | |
|----------------------------|-------|
| 1 | 1st |
| 2 | 2nd |
| 3 | 3rd |
| 4 | 4th |
| 5 | 5th |
| 6 | 6th |
| 7 | 7th |
| 8 | 8th |
| 9 | 9th |
| 10 | 10th |
| 11 | 11th |
| 12 | 12th |
| 13 | 13th |
| 14 | 14th |
| 15 | 15th |
| 16 | 16th |
| 17 | 17th |
| 18 | 18th |
| 19 | 19th |
| 20 | 20th |
| 21 | 21st |
| 22 | 22nd |
| 23 | 23rd |
| 24 | 24th |
| 25 | 25th |
| 26 | 26th |
| 27 | 27th |
| 28 | 28th |
| 29 | 29th |
| 30 | 30th |
| 31 | 31st |
| 32 | 32nd |
| 33 | 33rd |
| 34 | 34th |
| 35 | 35th |
| 36 | 36th |
| 37 | 37th |
| 38 | 38th |
| 39 | 39th |
| 40 | 40th |
| 41 | 41st |
| 42 | 42nd |
| 43 | 43rd |
| 44 | 44th |
| 45 | 45th |
| 46 | 46th |
| 47 | 47th |
| 48 | 48th |
| 49 | 49th |
| 50 | 50th |
| 51 | 51st |
| 52 | 52nd |
| 53 | 53rd |
| 54 | 54th |
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| 57 | 57th |
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| 67 | 67th |
| 68 | 68th |
| 69 | 69th |
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| 81 | 81st |
| 82 | 82nd |
| 83 | 83rd |
| 84 | 84th |
| 85 | 85th |
| 86 | 86th |
| 87 | 87th |
| 88 | 88th |
| 89 | 89th |
| 90 | 90th |
| 91 | 91st |
| 92 | 92nd |
| 93 | 93rd |
| 94 | 94th |
| 95 | 95th |
| 96 | 96th |
| 97 | 97th |
| 98 | 98th |
| 99 | 99th |
| 100 | 100th |

A – Ambient sampling for PAMS

Ad – Ambient sampling and duplicate for PAMS

Ab – Ambient sampling and trip blank

- one point flow check

| Table 3(b): PAMS Intensive(3-hour) Sampling Schedule | | | | | |
|---|--------|------------|--------|------------|--------|
| June | | July | | August | |
| Date | Sample | Date | Sample | Date | Sample |
| 05/29/2006 | Ad,# | 07/01/2006 | A | 08/03/2006 | Ad# |
| 06/01/2006 | A | 07/04/2006 | Ad | 08/06/2006 | Ab |
| 06/04/2006 | Ab | 07/07/2006 | A | 08/09/2006 | A |
| 06/07/2006 | Ad | 07/10/2006 | Ab | 08/12/2006 | Ad |
| 06/10/2006 | A | 07/13/2006 | A | 08/15/2006 | Ab |
| 06/13/2006 | A | 07/16/2006 | Ad,# | 08/18/2006 | A |
| 06/16/2006 | Ad | 07/19/2006 | A | 08/21/2006 | Ad |
| 06/19/2006 | A | 07/22/2006 | A | 08/24/2006 | A |
| 06/22/2006 | A | 07/25/2006 | Ad | 08/27/2006 | A |
| 06/25/2006 | Ad | 07/28/2006 | A | 08/30/2006 | Ad |
| 06/28/2006 | Ab | 07/31/2006 | A | | |
| Sampling Schedule Code Key A – Ambient sampling for PAMS Ad – Ambient sampling and duplicate for PAMS Ab – Ambient sampling and trip blank # - one point flow check | | | | | |